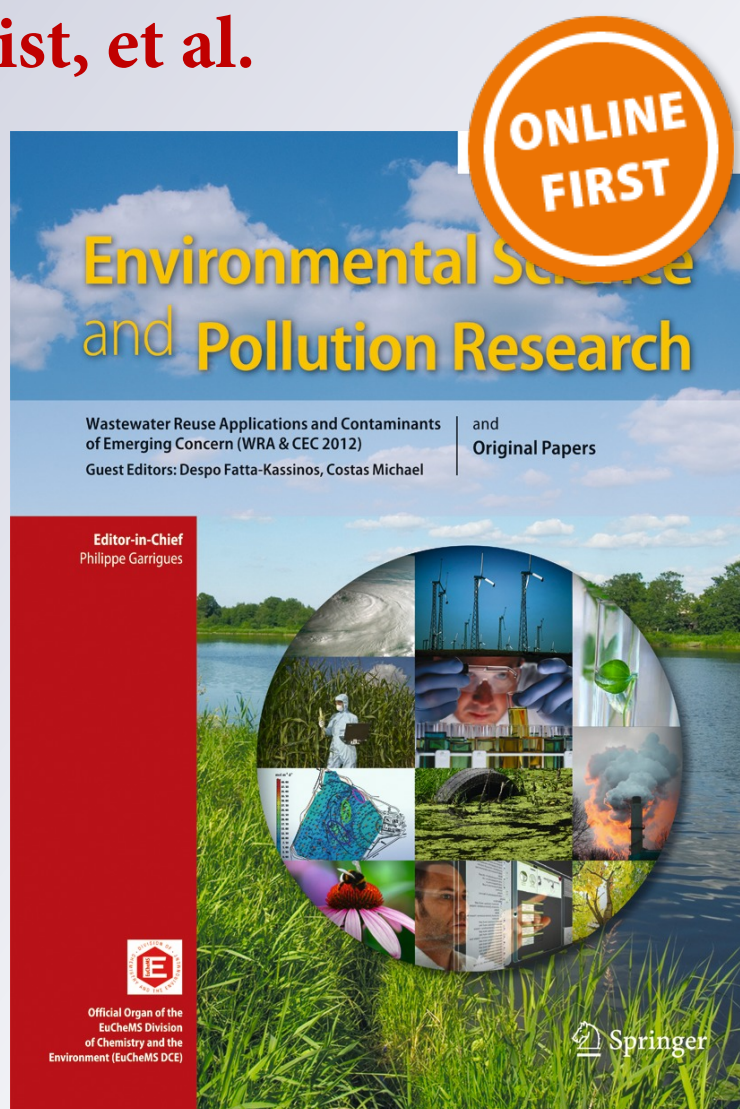# Utilisation of chemically stabilized arsenic-contaminated soil in a landfill cover

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RESEARCH ARTICLE

Utilisation of chemically stabilized arsenic-contaminated soil in a landfill cover

Jurate Kumpiene · Paolo Desogus · Sven Schulenburg · Mariarita Arenella · Giancarlo Renella · Evelina Brännvall · Anders Lagerkvist · Lale Andreas · Rolf Sjöblom

Abstract The aim of the study was to determine if an As-contaminated soil, stabilized using zerovalent iron (Fe^0) and its combination with gypsum waste, coal fly ash, peat, or sewage sludge, could be used as a construction material at the top layer of the landfill cover. A reproduction of 2 m thick protection/vegetation layer of a landfill cover using a column setup was used to determine the ability of the amendments to reduce As solubility and stimulate soil functionality along the soil profile. Soil amendment with Fe^0 was highly efficient in reducing As in soil porewater reaching 99 % reduction, but only at the soil surface. In the deeper soil layers (below 0.5 m), the Fe treatment had a reverse effect, As solubility increased dramatically exceeding that of the untreated soil or any other treatment by one to two orders of magnitude. A slight bioluminescence inhibition of *Vibrio fischeri* was detected in the Fe^0 treatment. Soil amendment with iron and peat showed no toxicity to bacteria and was the most efficient in reducing dissolved As in soil porewater throughout the 2 m soil profile followed by iron and gypsum treatment, most likely resulting from a low soil density and a good air diffusion to the soil. The least suitable combination of soil amendments for As immobilization was a mixture of iron with coal fly ash. An increase in all measured enzyme activities was observed in all treatments, particularly those receiving organic matter. For As to be stable in soil, a combination of amendments that can keep the soil porous and ensure the air diffusion through the entire soil layer of the landfill cover is required.

Keywords Immobilisation · Zerovalent iron · Amendments · Enzyme activity · Toxicity

Introduction

Several old landfills in the EU are being closed and covered following the EU Landfill Directive 99/31/EG. This requires millions of tons of construction materials including natural sand, gravel, and soil. At the same time, thousands of tons of contaminated soil are being excavated during remediation work and disposed of in landfills, with large volumes of clean soil needed to restore the remediated sites.

The demand for soil as cover material for landfills may be satisfied by replacing clean soils with contaminated ones that would otherwise be disposed of in a landfill. In such case, the contaminated soils need to be treated to avoid negative impacts on the surrounding environment. Various soil organic and inorganic amendments may be used for the stabilization or immobilization of trace elements (TE), so as to decrease their mobility and bioavailability through chemical reactions leading to TE sorption, complexation and (co)precipitation (Adriano et al. 2004).

Arsenic (As) is among the priority contaminants in Sweden; therefore, As contaminated sites are among the first to be remediated. Arsenic is a redox-sensitive element with a higher mobility at low redox conditions. The placement of As-

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contaminated soils in an anaerobic landfill can substantially increase the risks of As remobilization due to reductive dissolution of the main As-binding phases such as iron (Fe) oxides (Pedersen et al. 2006). Previous studies showed that As leaching can increase tenfold within few weeks in water-saturated (reduced) soil (Kumpiene et al. 2009). An appropriate use of soil as landfill top cover may prevent anoxic conditions, and As mobility in soil may be further reduced by Fe amendments (Kumpiene et al. 2009; Hartley and Lepp 2008; Nielsen et al. 2011). However, sole additions of Fe do not improve the soil capability to sustain vegetation grow and usually does not lead to any recovery of soil functions. The use of nutrient rich industrial residues (e.g., fly ash, biosolids, compost) as co-amendments and soil conditioners may improve soil biological activity and fertility (Mench et al. 2006; Ruttens et al. 2006; Renella et al. 2008; Kumpiene et al. 2009), as well as reduce As transfer to soil mesofauna (Coeurdassier et al. 2010).

The aim of this study was to determine if an As-contaminated soil, stabilized using zerovalent Fe (Fe^0) and its combinations with soil-conditioning materials (gypsum waste, coal fly ash, peat, or sewage sludge) could be used as a construction material at the top layer of the landfill cover. The As mobility and soil chemical and biochemical properties were monitored using an experimental set up reproducing a 2-m thick protection/vegetation layer of a landfill cover to determine the ability of the used amendments to reduce As solubility and stimulate soil functionality along the soil profile.

Materials and methods

Soil

Soil from a former wood impregnation site in Northern Sweden, contaminated by the use of CCA chemical K33 containing 34 % pentavalent As (as As_2O_5), 17 % divalent Cu (as CuO), and 27 % hexavalent Cr (as CrO_3), was collected from a landfill to which it was previously transported and stored in piles after remediation of the site by excavation. The soil was subsampled using fractional shoveling (Petersen et al. 2004), air-dried, homogenized, and sieved to <2 mm prior to characterization (Table 1).

Soil As and metal concentrations were determined by digesting 1 g of soil in 10 ml aqua regia (HCl–HNO₃, 3:1, v/v) using microwave digester (MARS 5, CEM). Metal concentrations were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES; Optima 2000 DV, Perkin Elmer). Soil pH, oxidation–reduction potential (Eh), and electrical conductivity (EC) were measured in 1:2 soil-double distilled water suspensions. Soil texture was determined using the hydrometer

Table 1 Main characteristics of the soil. Mean values±standard deviation, $n=3$

Property	Value
pH (1:2 H_2O)	6.02±0.01
Electrical conductivity (EC) ($\mu S\ cm^{-1}$)	439±26
Oxidation–reduction potential (Eh) (mV)	278±20
Total organic carbon (TOC) (%)	0.95±0.18
Cation exchange capacity (CEC) ($cmol\ kg^{-1}$)	5.04±0.26
Water holding capacity (WHC) (%)	29.2±0.4
Texture (sandy loam)	
Sand (%)	69.5
Silt (%)	28.5
Clay (%)	2.0
Elements (total concentration) ($mg\ kg^{-1}$ dw)	
As	254±17
Ca	7337±521
Cr	62±11
Cu	15±0.2
Fe	10 306±687
Mn	330±29
S	67±11
Zn	133±7

method (SS 027124, 1992) and total cation exchange capacity by the ammonium acetate method (Lavkulich 1981). Water holding capacity (WHC) was estimated from the mass of water remaining in drained soil after the saturation. Soil total organic carbon (TOC) was determined using a TOC analyzer (TOC-V CPH/CPN, Shimadzu) after removal of inorganic carbon (IC) by concentrated HCl. The remaining carbon was oxidized at 900 °C, and the formed CO_2 was analyzed by non-dispersive infrared absorbance.

Amendments

The fly ashes from coal and wood combustion (CFA) were obtained from Öresundskraft (Sweden); the sewage sludge (SS) was obtained from Uddebo waste water treatment plant (Sweden). Gypsum boards (G) and commercially available natural peat (P) were obtained from local suppliers in Sweden, and zerovalent iron grit (Fe^0), containing 97 % Fe^0, from Wheelabrator (Allevard Enterprise, France). Organic matter content of the amendments was determined by loss on ignition at 550 °C, and main properties of the amendments are reported in Table 2.

Soil–amendment mixtures

Five batches of 40 kg of soil were mixed with amendments and homogenized for 15 min in a cement mixer to reach an

Table 2 Main properties of the amendment materials

Property	Iron grit (Fe)	Gypsum (G)	Coal fly ash (CFA)	Peat (P)	Sewage sludge (SS)
pH (1:2 H_2O)	n.d.	7.9	12.4	3.9	7.9
Electrical conductivity (mS cm^{-1})	n.d.	2.4	20.0	0.1	5.1
Moisture content (%)	n.d.	18	1	57	80
Organic matter (%)	n.d	7.0	6.0	94.3	60.8
Average particle size (μm)	<100	n.d.	6.9	n.d.	n.d.

n.d. not determined

even distribution. In total, five treatments were prepared: soil+1 % Fe, soil+1 % Fe+3 % CFA, soil+1 % Fe+10 % G, soil+1 % Fe+5 % P, and soil+1 % Fe+5 % SS. Nonamended soil was used as control. The WHC of amended soils was determined as described above, and distilled water was added to all mixtures to reach 20 % of WHC.

Batch leaching test

A standard two-step compliance batch leaching test (EN 12457-2) at a liquid to solid ratio (L/S) 10 was used to estimate leachable concentrations of As and metals in the untreated and amended soils. For the leaching tests, triplicate subsamples of 0.2 kg from each soil was suspended in deionised water to reach L/S 10 and shaken for 24 h using a rotating device. The eluates were filtered over 0.45-μm nitrocellulose membrane filter and analyzed for As and metals. The leached concentrations expressed in milligrams per kilograms dry weight were compared to the leaching limit values for waste acceptance at EU landfills (2003/33/EC Annex II).

Column test

The column test was designed to simulate a combined vegetation and protection layer of a landfill cover. The homogenized amended soils were packed into columns consisting of four stacked 50-cm segments (total height, 200 cm, Ø 70 mm) and equipped with soil moisture samplers at depths of 45, 95, and 195 cm, thereof called top, middle, and bottom layers. One-centimeter sand filters and textile filters were placed at the bottom of the columns to prevent particle wash out. Each column contained 8–11 kg dw soil. Three columns were prepared for each of the soil mixtures and the untreated soil (control samples). The soil density in each column was estimated using the middle segment immediately after filling the columns and at the end of the experiment.

Distilled water was added at the top of each column at six times with 2 weeks in between the adjacent additions. The amount of added water corresponded to the amount removed by sampling (about 300 ml). The percolation was gravity driven. The columns were left for 1 year, and the same procedure was repeated. The soil humidity level was controlled by weighing the columns and adjusted to the initial saturation value of 20±3 % before the second porewater sampling.

Analysis of soil porewater

Soil porewater was sampled from the top, middle, and bottom segments using Rhizon soil moisture samplers (Eijkelkamp, The Netherlands) in acid-washed and vacuumed 100 ml glass bottles after 2–3 days of equilibration following each H_2O addition to soil columns. An aliquot was immediately used for EC, redox, and pH measurements; the rest was stored at 4 °C for 1–3 weeks for elemental analysis by ICP-OES, dissolved organic carbon (DOC) and sulfates by a spectrophotometer (AACE Quaatro, Bran&Luebbe). Due to the insufficient amount of porewater generated after the first water addition, porewater from the first and the second samplings were pooled into one sample. The samples were numbered, where the first number indicates the sampling year and the second number shows the sampling week (1.1, 1.3, 1.5, 1.7, 1.9, 2.1, 2.3, 2.5, 2.7, 2.9, and 2.11). In eluates, mainly from the bottom layer of soil+Fe, Fe-bearing precipitates were observed. The subsample of the eluate with precipitates was filtered through 0.45-μm syringe filters, and the precipitates in the remaining part were dissolved in a thermal bath (85 °C) with 2 % HCl prior to the elemental analysis. The filtered samples were also used for DOC determination.

Analysis of soil solid phase

After the porewater sampling, the columns were weighed and dismantled, and soil samples were collected from the top (45 cm), middle (95 cm), and bottom layers (195 cm) for determination of total element concentrations, enzyme activities, and soil organic matter humification degree.

The total element concentrations were measured using inductively coupled plasma mass spectrometry and ICP-AES by the accredited laboratory ALS Scandinavia AB,

Sweden, after dissolution in 5 ml conc. HNO_3+0.5 ml H_2O_2 using a microwave.

Soil organic matter humification

The total extractable C (TEC) was measured by wet oxidation of 0.5 M K_2SO_4 extracts with $K_2Cr_2O_7$ in acidic conditions and spectrophotomeric determination of Cr^{3+} at 600 nm (Soon and Abboud 1991). Soil humic substances were extracted using 0.1 M NaOH+0.1 M $Na_4P_2O_7$ solution at 65 °C. The slurries were centrifuged at 5,000×g and filtered at 0.20 μm (Millipore, Billerica, USA; TEC). Humic acids (HAs) were separated from the fulvic acids (FAs) by precipitation after acidification at pH<2. The C content of HA and FA fractions were determined by $K_2Cr_2O_7$ wet oxidation, and the humification degree percent (HD%) was calculated from the formula [(HA+FA)/TEC]× 100 (Ciavatta et al. 1990).

Soil toxicity and biochemical analyses

Soil toxicity was assessed by the BioTox™ method (Lappalainen et al. 1999) based on the luminescence inhibition of the *Vibrio fischeri* bacterium (Aboatox Oy, Turku, Finland) according to the ISO standard method (ISO 11348-3, 1998), using a Sirius luminometer (Berthold Detection Systems, Pforzheim, Germany).

Soil microbial biomass was estimated by the adenosine triphosphate (ATP) content that was determined according to Ciardi and Nannipieri (1990). The acid and alkaline phosphomonoesterase activities were assayed according to Tabatabai and Bremner (1969), the arylesterase activity according to Zornoza et al. (2009), the β-glucosidase activity according to Tabatabai (1982), and the urease activity activity according to Nannipieri et al. (1974). The soil dehydrogenase activity was measured by using INT as substrate according to Trevors (1984). Concentrations of *p*-nitrophenol (*p*-NP) produced in the assays of acid and

alkaline phosphomonoesterase, arylesterase, and β-glucosidase activities were calculated from a *p*-NP calibration curve after subtraction of the absorbance of the controls at 400 nm wavelength, whereas the INT-formazan (INTF) produced by the dehydrogenase activity was spectrophotometrically measured using a standard curve in methanol at 480 nm, after subtraction of the absorbance of the respective controls. The NH_4^+ produced by urease activity was colorimetrically determined using the Nessler reagent at 436 nm and a calibration curve based on ammonia standards.

Statistics

A *t* test was used to compare the means of sample pairs to determine statistically significant differences among the sample means at 95 % confidence level. Regression analysis using a linear model was used to determined correlation coefficients and R^2 values using the software Statgraphics Plus 5.1.

Results

Properties of soil and mixtures

All amendment combinations significantly increased soil WHC (Table 3). Soil density was also affected: addition of gypsum, peat, and sludge in combination with iron significantly decreased soil density, iron alone had no effect on soil density, while addition of ash increased it compared with the untreated soil.

Total element concentration in columns

The addition of amendments did not increase the total As concentration in any of the treated samples (Table 4). After 2 years since the experiment setup, soil As concentration significantly decreased only in the middle layers of Fe and

Table 3 Water holding capacity (WHC) of soil-amendment mixtures and soil density in columns

	OM[a] %	SD	WHC %	SD	Initial density g cm^{-3}	SD	End density	SD
Untreated soil	1.76	0.20	29.2	0.4	1.31	0.03	1.29	0.13
Soil+Fe	1.88	0.06	29.2	0.5	1.32	0.03	1.43	0.11
Soil+Fe+G	2.23	0.28	46.4	1.6	1.12	0.03	1.09	0.03
Soil+Fe+CFA	2.04	0.07	31.7	0.5	1.36	0.01	1.38	0.05
Soil+Fe+P	6.92	0.77	51.4	2.5	0.97	0.02	0.88	0.02
Soil+Fe+SS	4.53	0.27	59.5	1.6	1.14	0.03	0.96	0.03

Standard deviation (SD), n=3

Fe zerovalent iron, *G* gypsum, *CFA* coal fly ash, *P* peat, *SS* sewage sludge

[a] Organic matter (OM) content was estimated by loss on ignition at 550 °C

Table 4 Concentration of As, Fe, and S in soil at the end of the experiment sampled in three soil layers (mg kg^{-1} dw)

Soil treatment	Column layer	As mg kg^{-1}	SD	Fe	SD	S	SD
Untreated soil	Top	249	8	10,090	573	54	4
	Middle	254	21	10,527	1,160	71[a]	7
	Bottom	259	23	10,300	265	77[a]	2
Soil+Fe	Top	235	13	21,433	2,043	74	11
	Middle	201[a]	7	18,533	1,002	64	7
	Bottom	218	5	18,267	577	75	7
Soil+Fe+G	Top	240	48	17,467	1,747	14,900	4,557
	Middle	211	7	18,500	854	15,800	2,700
	Bottom	201	8	16,900	2,081	14,767	1,890
Soil+Fe+CFA	Top	212	16	19,500	1,572	162	63
	Middle	235	35	21,467	4,100	274	97
	Bottom	207	7	19,967	1,626	307[a]	43
Soil+Fe+P	Top	222	12	17,733	1,893	167	20
	Middle	220	13	17,833	451	173	21
	Bottom	213	28	19,067	1955	193	27
Soil+Fe+SS	Top	204	11	17,733	850	320	42
	Middle	186[a]	1	15,567[a]	404	558[a]	149
	Bottom	200	15	16,467	833	454[a]	1

Standard deviation (SD) of three replicates

[a] Values that significantly differ from those in the top layer of the same columns at 95 % confidence level

Fe+SS treatments, whereas the Fe concentration did not change regardless of soil treatment or layer (Table 4).

Sulfur concentration significantly increased in the middle and bottom layers of the untreated soil and soil with Fe+SS, and in the bottom layer of the soil with Fe+CFA (Table 4).

Leaching of arsenic in soil

Arsenic leaching significantly decreased in all soil treatments as compared to the untreated soil, except for the Fe+CFA treatment (Table 5). The lowest leaching value was achieved in Fe+G and Fe+P treatments. Slightly higher leaching values were observed in the Fe and Fe+SS treatments, with comparable levels. Arsenic leaching in these four treatments was below the leaching limit value for waste

Table 5 Arsenic concentration, pH, and electrical conductivity (EC) in leachates (L/S10) of untreated soil and soil treated using zerovalent iron (Fe), gypsum (G), coal fly ash (CFA), peat (P), sewage sludge (SS)

	As mg kg^{-1} DW	SD	pH –	SD	EC µS cm^{-1}	SD
Untreated soil	1.23	0.05	5.9	0.0	115	8
Soil+Fe	0.08	0.01	6.5	0.2	80	5
Soil+Fe+G	<0.04		7.2	0.1	2,233	32
Soil+Fe+CFA	4.79	0.28	8.5	0.2	336	11
Soil+Fe+P	<0.04		6.0	0.1	113	3
Soil+Fe+SS	0.06	0.06	6.6	0.0	286	2

Standard deviation (SD), $n=3$

acceptable at inert waste landfills (i.e., 0.5 mg kg^{-1}). By contrast, addition of CFA significantly increased As leaching (4.8±0.3 mg kg^{-1}) to the levels that exceeded the leaching limits for waste acceptable at landfills for non hazardous waste (i.e., 2 mg kg^{-1}).

Arsenic in soil porewater

In the untreated soil, concentration of dissolved As in soil porewater gradually increased at the top and the middle layers from 0.06±0.002 mg L^{-1} and 0.07±0.002 mg L^{-1} in the beginning to 0.25±0.02 mg L^{-1} and 0.19± 0.07 mg L^{-1} at the end of the sampling period, respectively (Fig. 1a). Dissolved As concentration in the bottom layer was on average lower than in the above layers and did not significantly change over time.

Dissolution of As in Fe amended soil decreased at the top layer from initial concentrations of 0.013±0.006 mg L^{-1} to undetectable levels during the last three samplings, whereas As dissolution in the middle and the bottom layers significantly increased and reached the highest values among the treatments (Fig. 1b).

The Fe+G treatment decreased As solubility in all soil layers as compared to the untreated soil (Fig. 1c), with the highest values in the deepest layers. The As solubility on average was one of the lowest among the soil treatments.

Similarly to the batch leaching results, Fe+CFA treatment increased As solubility in the columns by doubling the values during the second year of sampling, particularly in the bottom layers (Fig. 1d).
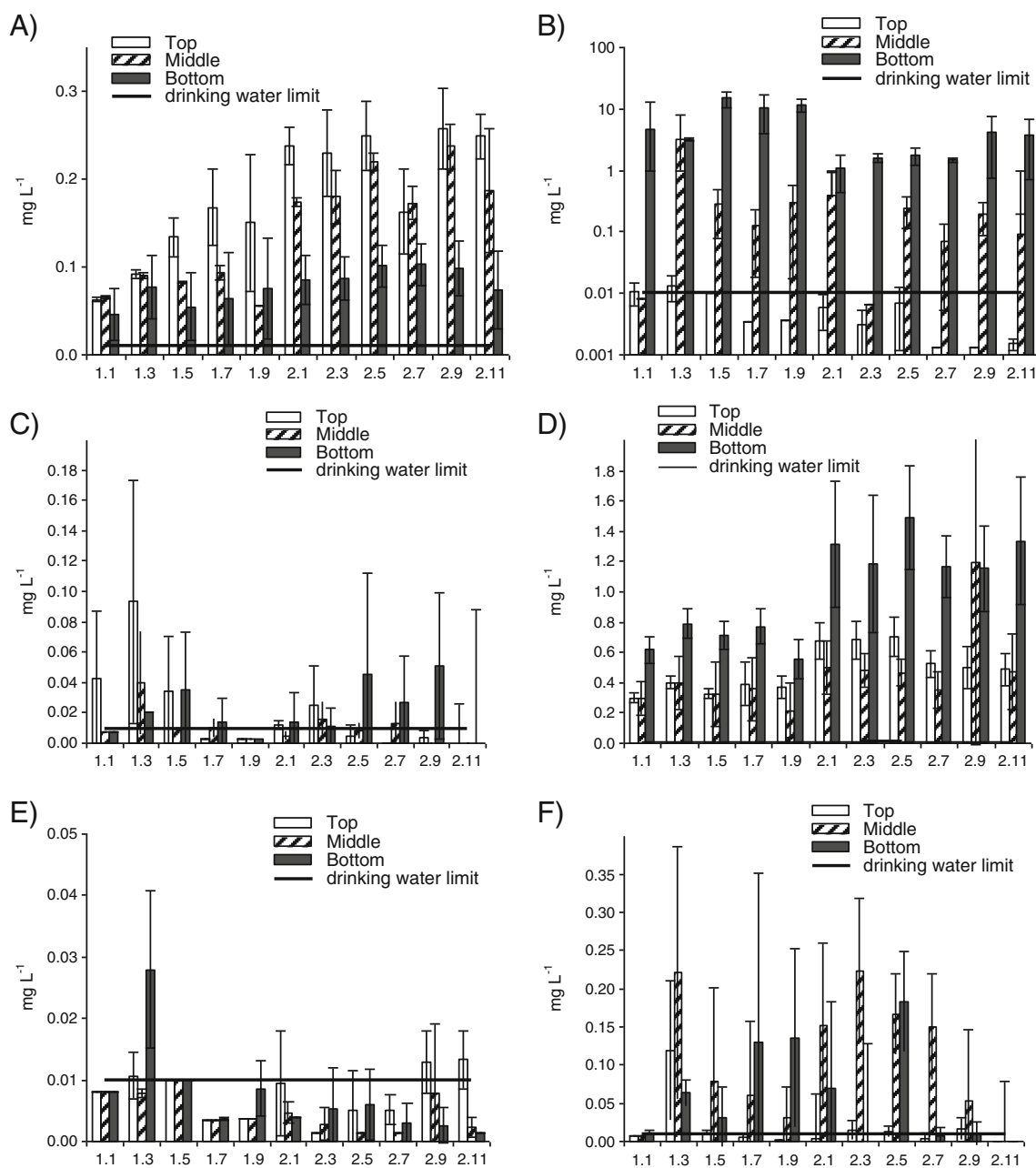
Fig. 1 Concentration of As in soil porewater collected at the top, middle and bottom of the columns containing **a** untreated soil (control), **b** soil+Fe (logarithmic scale), **c** soil+Fe+gypsum, **d** soil+Fe+coal fly ash, **e** soil+Fe+peat, and **f** soil+Fe+sewage sludge. The error bars indicate the standard deviations of the means ($n=3$). Limit for arsenic in drinking water (0.01 mg L^{-1}) is given for comparison. *X-axis* The first number indicates the sampling year and the second number shows the sampling week

The lowest dissolved As concentration among the treatments was measured in Fe+P soil. Except for one deviating value measured during the first year in the bottom layer (sampling point 1.3, Fig. 1e), concentration of dissolved As was close to or below the As limit value in drinking water (0.01 mg L^{-1}) established by the World Health Organisation (1993).

The concentration of dissolved As in Fe+SS treatment varied considerably during the sampling period and showed higher values in the middle layer (Fig 1f).

Iron in soil porewater

In the control soil, Fe was detectable only in the bottom layer during the first year at concentrations between 0.01 and 0.25 mg L^{-1}, whereas in the above layers, Fe concentrations were close or below the instrument detection limit. A similar trend was observed in Fe+G, where detectable Fe concentrations were measured in the bottom layer, although in higher concentrations than in the untreated soil (0.4–103 mg L^{-1}).

Except for few individual values, no detectable concentrations of dissolved Fe were measured in porewater of Fe+CFA and Fe+P treatments. Dissolved Fe in Fe+SS was detected in all layers during the first year and only in the middle and bottom layers during the second year. The values were slightly higher than in the control soil and varied between 0.015 and 1.7 mg L^{-1} at the top, 0.7 and 4.9 mg L^{-1} in the middle, and 0.18 and 3.5 mg L^{-1} at the bottom layers.

The highest porewater Fe concentration was measured in soil amended with Fe alone, but only in the middle and bottom layers. In the middle layer, dissolved Fe varied between 138 and 278 mg L^{-1} during the first year, then substantially decreased and varied between 0.8 and 10.6 mg L^{-1} during the second year. In the bottom layer, Fe concentration increased from 220 to 785 mg L^{-1} during the first year, then decreased and leveled off at ca 250±24 mg L^{-1} during the second year. At the top layer, dissolved Fe was undetectable in nearly all samples.

During the porewater sampling in the middle and at the bottom of soil+Fe columns, changes in solution color and formation of orange-colored precipitates was observed. Differences in As and Fe concentrations between the filtered and HCl-dissolved samples were substantial, i.e., samples with dissolved precipitates contained three to four orders of magnitude higher As and Fe concentrations than the filtered samples. The former concentrations were included into the subsequent data analysis.

pH, oxidizing–reducing potential, and electrical conductivity of soil porewater

The pH of the porewater of the control soil varied over two pH units (from 5 to 7) and stabilized around pH 6 at the top and middle layers and just above pH 5 at the bottom during the second year (Fig. 2a). The largest pH variation was observed in soil amended with Fe alone, with pH values 5–6 at the bottom and 4.6–8 in the middle layer. The pH at the top increased from 6.2 to 7.4 in the beginning and then gradually decreased to around 6.5 during the second year. The porewater pH values of the Fe+G treatment varied between 7 and 8 in all layers over the 2-year measurements. The highest pH values were measured in Fe+CFA treatment (pH 8–9) with relatively small differences among the sampling times and layers, although the pH at the bottom were on average 0.5 pH unit higher than in the middle and top layers. The pH of Fe+P treatment was similar to those of the untreated soil during the first year and decreased over time to values of 5.5–5.7 in all soil layers. The pH in the porewater of Fe+SS treatment was similar to that of Fe+G with decreasing values going from the top (6.7–

8.2) to the middle (pH 7.6–8.7) and the bottom layers (pH 8.4–8.9). During the second year, the pH value in the middle layer became similar to that of the top layer (at 7.5±0.4).

The redox values were similar in control soil and soil containing Fe+P (110–300 mV and 120–320 mV, respectively) and were on average the highest among the treatments (Fig. 2b). Redox potential in all the other soils had similar trends, with decreasing values over time (from 150–200 mV to 35–70 mV) and lower average values in the bottom layers. Only during the last sampling, the redox in the top layer of Fe+G soil significantly dropped below the values of the middle and the bottom layers. The Fe+P treatment showed the most stable redox potential throughout the experiment with no redox decrease trends in the middle or bottom layers, as it was observed in the other treatments.

The electrical conductivity (EC) values differed between the treatments in the beginning of the experiment, but were similar in all soil layers within each treatment (Fig. 2c). Differences between the layers developed over time to various extents in all treatments, especially in control soil, Fe, and Fe+SS treatments and slightly less in Fe+P treatment. The EC became significantly higher in the bottom layers of these mixtures. The Fe+G and Fe+CFA treatments initially showed a more uniform EC between soil layers, but significantly increased in the bottom layer at the end of the experiment. The Fe+SS treatment showed the highest EC values among the treatments, especially in the bottom layers. Control soil and Fe treatment had similar and uniform EC values during the first year, while the EC dropped at the top and middle layers and significantly increased at the bottom layer during the second year.

Dissolved organic carbon in soil porewater

Concentration of DOC in porewater of control soil was lower in the top and middle layers than in the bottom, but differences between the layers became insignificant over time (Fig. 3a). Soil amendment with Fe changed DOC distribution in the soil. At the top layer, DOC concentration was stable during the experimental period and significantly lower than in the top layer of the untreated soil. DOC in the middle and the bottom layers of soil+Fe were similar and higher than in the top layer and all the untreated soil layers (Fig. 3b). DOC in the bottom layer significantly increased over time, while in the middle of the columns, the values decreased. Concentration of DOC in Fe+G treatment was similar in the top and middle layers, with higher values and larger variability at the bottom than at the top and middle layers (Fig. 3c). Concentration of DOC in porewater of soil with Fe+CFA was significantly higher than in the untreated
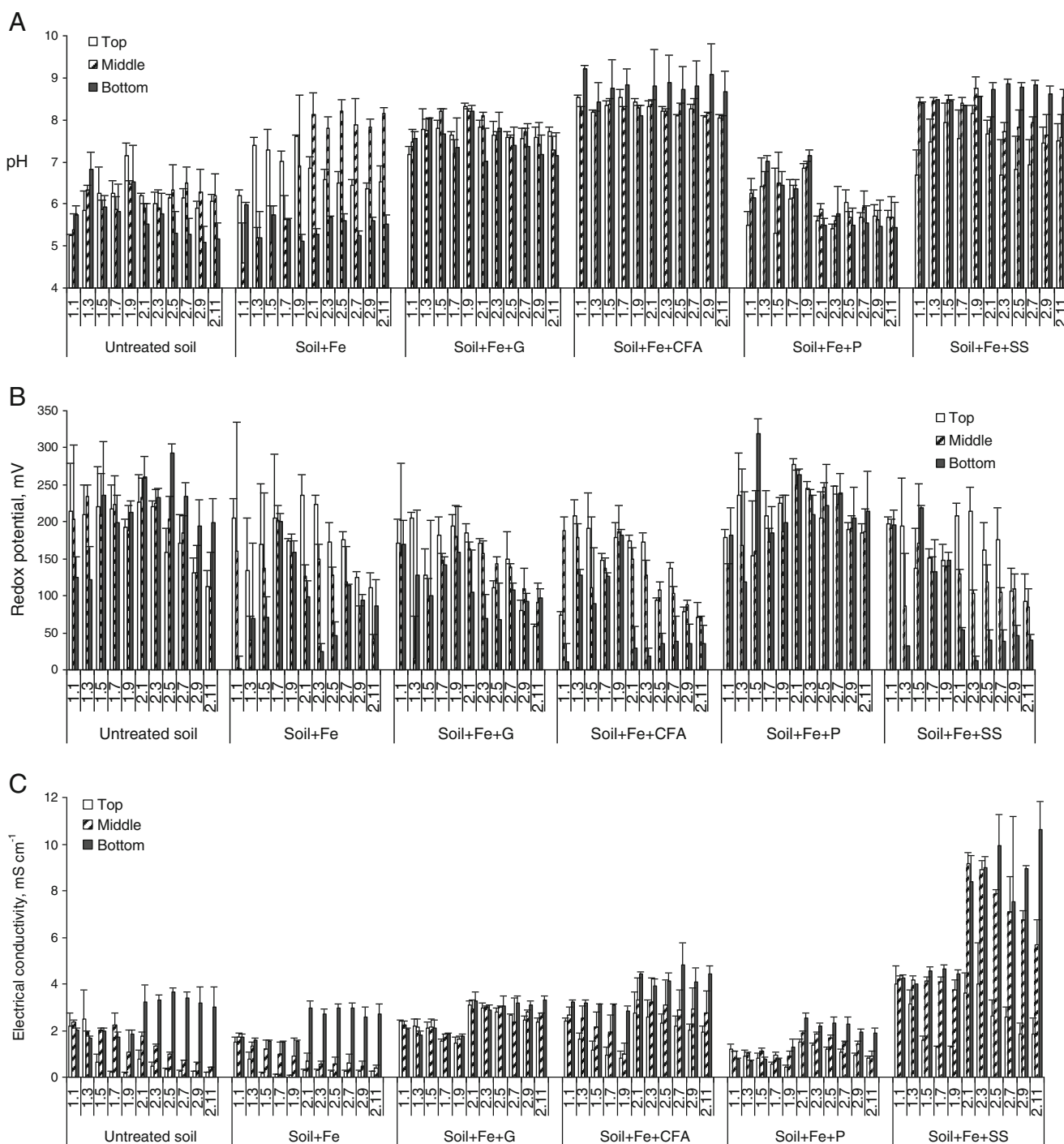
Fig. 2 **a** pH, **b** redox potential, and **c** electrical conductivity of porewater collected at the top, middle, and bottom of the columns containing untreated soil (control) and soil with various amendments. The *error bars* indicate the standard deviations of the means (*n*=3). *X-axis* The first number indicates the sampling year and the second number shows the sampling week

soil in all layers (Fig. 3d) with a gradual decrease in the top and middle layers and an initial increase followed by a slight decrease in the bottom layer over the experimental period. The Fe+P treatment showed the lowest DOC concentrations in soil porewater, with similar values at the top and middle layers during the first year, followed by an increase and then

a gradual decrease during the second year (Fig. 3e). The DOC concentration at the bottom was significantly higher than in the above layers during the first year, followed by some variations during the second year and stabilization at values close to those of the upper layers. The Fe+SS treatment showed the highest DOC concentrations among the
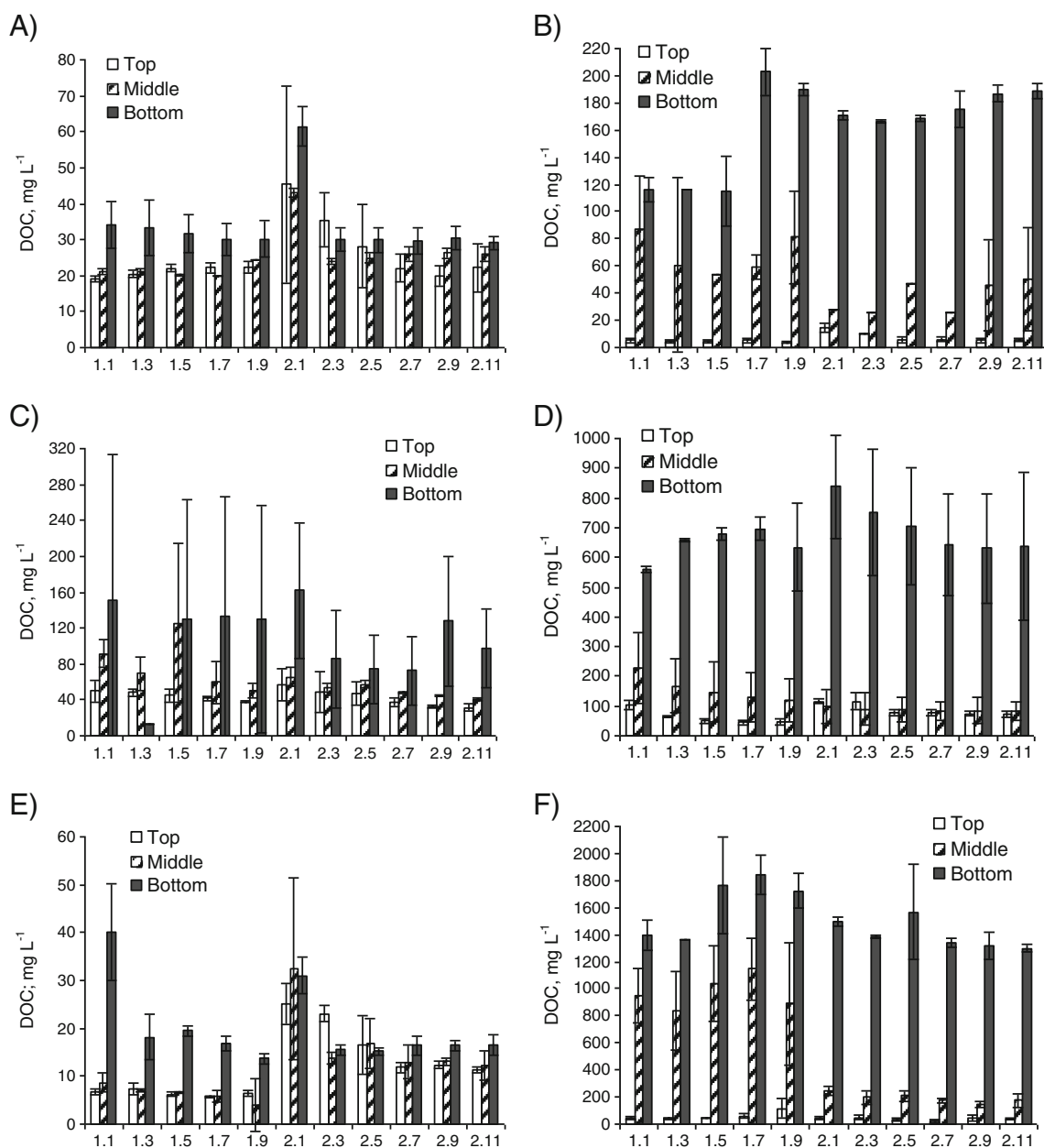
Fig. 3 Concentration of dissolved organic carbon (*DOC*) in soil porewater collected at the top, middle, and bottom of the columns containing **a** untreated soil (control), **b** soil+Fe, **c** soil+Fe+gypsum, **d** soil+Fe+coal fly ash, **e** soil+Fe+peat, and **f** soil+Fe+sewage sludge. The *error bars* indicate the standard deviations of the means (*n*=3). *X-axis* The first number indicates the sampling year and the second number shows the sampling week

treatments (Fig. 3f) with the highest values at the bottom, followed by the middle and then the top layers.

Sulfates in soil porewater

The Fe+G treatment showed the highest concentration of sulfates in porewater with a uniform distribution among the soil layers (Table 6). Slightly lower sulfate concentrations were measured in Fe+CFA treatment and in the middle layer of Fe+SS treatment. The lowest porewater sulfate concentrations were found in Fe and

Fe+P treatments. The largest variation in the sulfate concentrations among soil layers were observed in Fe+SS treatment, with values in the bottom layer being by one to two orders of magnitude lower than in the top and middle layers (Table 6).

Soil organic matter humification

Significant differences in FA and HA concentrations were only found in the untreated soil, with an accumulation of FA at the bottom and of HA at the top layers of the soil

Table 6 Concentration of sulfates in soil porewater during the second year of the experiment sampled at three soil column layers (mg L^{-1})

Column layer	Time, week	Soil		Soil+Fe		Soil+Fe+G		Soil+Fe+CFA		Soil+Fe+P		Soil+Fe+SS	
		SO_4^{-2} mg L^{-1}	SD	SO_4^{-2}	SD	SO_4^{-2}	SD	SO_4^{-2}	SD	SO_4^{-2}	SD	SO_4^{-2}	SD
top	2.1	95	[a]	33	15	1,186	33	853	261	12	2	580	202
	2.3	55	11	28	11	1,512	132	606	290	12	2	496	97
	2.5	67	14	29	8	1,390	294	618	242	14	4	429	156
	2.7	51	11	29	7	1,148	22	479	321	14	3	472	132
	2.9	38	8	31	8	1,194	43	411	202	15	2	346	315
	2.11	34	8	31	8	1,273	378	380	293	18	1	470	128
middle	2.1	110	1	6.9	[a]	1,212	4	1,085	116	10	5	1,634	496
	2.3	112	7	4.5	[a]	1,753	709	906	311	10	6	1,112	546
	2.5	173	11	7.9	[a]	1,166	10	1,014	162	10	6	1,326	418
	2.7	170	23	5.1	[a]	1,107	8	935	146	10	6	1,241	401
	2.9	143	34	4.9	1.7	1,185	45	727	570	11	6	1,153	399
	2.11	112	6	5.6	3.4	827	683	922	219	12	7	892	189
bottom	2.1	142	33	3.6	0.4	1,498	431	1,178	15	10	2	46	14
	2.3	134	42	4.2	0.9	1,594	142	1,154	33	11	3	21	5
	2.5	146	32	4.2	0.1	1,420	412	1,059	166	10	3	18	5
	2.7	177	6	4.7	0.6	1,399	388	1,154	21	9	3	22	2
	2.9	189	2	5.2	0.9	1,587	336	1,196	32	12	4	ND	
	2.11	191	9	4.0	0.6	1,638	391	1,196	45	12	6	19	[a]

Standard deviation (SD), $n=3$

[a] Only one replicate was analyzed due to insufficient amount of other samples

ND not determined

columns (Table 7). Although a general trend of increase in TEC, FA, and HA, and a trend of decrease in the HD% was observed, no significant differences were found in relation to the treatments (Table 7).

Table 7 Concentration of total extractable C (TEC), humic acid C (HC), fulvic acid C (FC), and humification degree percent (HD%) of soil treatments at the end of the experiment

Values in brackets are standard deviations of the means ($n=3$)

[a] Symbols indicate significant differences between top and bottom layers of the same treatments at 95 % confidence level

Soil treatment	Column layer	TEC	FA	HA	HD%
Untreated soil	Top	3,171 (186)	772 (93)	1,386 (211)	68.3 (10)
	Middle	2,945 (359)	1,333[a] (243)	1,105[a] (243)	83.6 (21)
	Bottom	2,967 (355)	1,561[a] (528)	898[a] (31)	83.2 (17)
Soil+Fe	Top	2,741 (392)	975 (100)	548 (87)	56.3 (7)
	Middle	2,454 (620)	1,162 (145)	537 (101)	71.9 (18)
	Bottom	2,663 (252)	960 (77)	707 (294)	62.8 (8)
Soil+Fe+G	Top	2,419 (139)	981 (159)	459 (34)	58.7 (5)
	Middle	2,600 (308)	837 (130)	388 (26)	47.2 (4)
	Bottom	2,530 (457)	798 (131)	584 (162)	54.8 (8)
Soil+Fe+CFA	Top	2,812 (669)	(709 (305)	1,127 (174)	64.0 (13)
	Middle	2,295 (244)	604 (33)	791 (160)	60.6 (3)
	Bottom	2,220 (102)	686 (176)	596 (62)	57.8 (7)
Soil+Fe+P	Top	11,365 (1240)	1,564 (263)	5,431 (501)	61.6 (4)
	Middle	11,188 (2039)	1,816 (75)	6,146 (832)	73.1 (16)
	Bottom	11,400 (746)	1,878 (232)	5,539 (1133)	65.1 (11)
Soil+Fe+SS	Top	4,868 (628)	1,662 (375)	1,809 (237)	72.0 (9)
	Middle	5,836 (987)	1,357 (286)	1,604 (215)	51.1 (4)
	Bottom	5,024 (222)	1,208 (847)	1,446 (274)	52.4 (9)

Soil toxicity and biochemical analyses

The highest soil toxicity was detected in the untreated soil and Fe+G treatment, with significantly higher values in the bottom layer in the latter treatment (Table 8). Slight bioluminescence inhibition was detected in the Fe treatment, whereas no inhibition could be detected in the Fe+CFA, Fe+P, and Fe+SS treatments.

The control soil showed very low values of ATP content, whereas a general increase in the ATP values was observed in all treatments, particularly Fe+SS and Fe+P, with the latter showing also significantly higher values in the top layer (Table 8).

Among the measured enzyme activities, a general increase in all values was observed in all treatments, particularly those receiving organic matter, with higher values in different soil layers depending on the enzyme activity and treatment (Table 8).

Discussion

Effect of soil amendments on arsenic immobilization

Soil amendment with Fe^0 was highly efficient in reducing As in soil porewater reaching 99 % reduction, but only in the top layer. In the deeper layers of soil+Fe columns, Fe treatment had a reverse effect, i.e., As solubility increased dramatically exceeding that of the untreated soil or any other treatment by one to two orders of magnitude. Increased As solubility in the deeper layers correlated well with the increased Fe dissolution and decreased redox potential. An explanation of such behavior could be that newly formed Fe oxyhydroxides from oxidation of Fe^0 are more susceptible to reductive dissolution in slightly reducing environment (at 35–100 mV) than Fe in untreated soil possibly dominated by more crystalline Fe phases. Formation of As-containing Fe precipitates in porewater suggests that colloidal Fe oxyhydroxides can sorb As and transport it to deeper soil layers under slightly reducing conditions. It is unclear, however, whether the colloids were formed in the columns or dissolved Fe precipitated during the sampling and reacted with As outside the columns. Oxidation and precipitation of Fe that is exposed to light has been shown to occur in solutions within few hours (Geroni et al. 2009). Porewater sampling took longer time, which gives a reason to assume that at least partial Fe oxidation occurred outside the columns. Regardless of the reason, the possible As migration to groundwater under slightly reducing conditions remains high.

Co-amendment of iron with peat sustained a relatively high redox potential throughout the column depth, likely due to the lower soil density, which facilitate the air

Table 8 Soil toxicity, enzyme activities, and ATP content in soil treatments at the end of the experiment

Soil treatment	Column layer	Soil toxicity [inhibition (%)]	Ac phosphatase (mg pnp kg^{-1} h^{-1})	Alk phosphatase	β-glucosidase	Arylesterase	Urease (mg NH$_4^+$–N kg^{-1} h^{-1})	DHase (mg INTF kg^{-1} h^{-1})	ATP (ng pnp kg^{-1} h^{-1})
Untreated soil	Top	21 (4)	94 (4)	12 (2)	74 (3)	100 (12)	2.4 (0.2)	1.5 (0.1)	43 (7)
	Middle	20 (3)	92 (17)	11 (1)	85 (8)	86 (9)	2.6 (0.2)	1.1 (0.5)	42 (6)
	Bottom	16 (5)	87 (10)	14 (2)	76 (4)	92 (8)	2.4 (0.5)	1.8 (0.4)	49 (6)
Soil+Fe	Top	6 (4)	113 (30)	13 (4)	72 (18)	114 (9)	1.3 (0.3)	1.7 (0.3)	92 (13)
	Middle	4 (2)	127 (53)	14 (2)	78(15)	98 (10)	1.9 (0.4)	2.0 (0.4)	85 (6)
	Bottom	2 (0.4)	118 (19)	19 (7)	77(12)	101 (8)	3.8 (1.1)	1.7 (0.1)	79 (14)
Soil+Fe+G	Top	7 (3)	137 (20)	48 (6)	100 (2)	184 (13)	3.2 (1.1)	3.3^a (0.4)	94 (5)
	Middle	10 (3)	130 (6)	59 (9)	97 (7)	156 (11)	5.5 (1.2)	3.6^a (0.7)	90 (7)
	Bottom	15^a (3)	135 (4)	62 (7)	92 (10)	144 (8)	4.9 (1.1)	2.3 (0.3)	88 (13)
Soil+Fe+CFA	Top	NI	40 (13)	133 (19)	42 (4)	198 (13)	6.9 (1.5)	3.5 (0.3)	108 (10)
	Middle	NI	56 (8)	94 (7)	40 (4)	201 (11)	10.8 (2.1)	3.9 (1.0)	96 (10)
	Bottom	NI	39 (7)	60 (7)	39 (8)	182 (8)	14.2^a (2.9)	4.2 (0.2)	96 (0.1)
Soil+Fe+P	Top	NI	379 (29)	22 (5)	213^a (28)	217 (8)	10.4 (2.1)	2.5^a (0.5)	243^a (29)
	Middle	NI	370 (61)	31 (5)	147 (7)	288^a (15)	24.4^a (4.3)	1.3 (0.1)	139 (13)
	Bottom	NI	321 (11)	26 (2)	138 (19)	260^a (16)	32.0^a (4.7)	0.9 (0.1)	147 (19)
Soil+Fe+SS	Top	NI	334^a (52)	141 (18)	353 (43)	767^a (39)	92.8^a (5.8)	32.7^a (5.1)	170 (26)
	Middle	NI	239 (34)	149 (12)	379 (20)	795^a (44)	287.2^a (14.3)	13.4 (1.2)	172 (16)
	Bottom	NI	274 (46)	190 (25)	327 (36)	603 (46)	15.7 (3.1)	13.1 (1.6)	175 (8)

Values in brackets are standard deviations of the means (*n*=3)

^{a} Symbols indicate significant differences between top and bottom layers of the same treatments at 95 % confidence level

NT no bioluminescence inhibition detected

diffusion through the soil column. Air supply to deeper soil layers implies both the stability of Fe oxides and Fe-bound As, as demonstrated by the high degree of As retention and extremely low Fe dissolution in this treatment. Visual inspection of the dismantled column segments showed that Fe oxidation occurred throughout the entire column depth, as indicated by the presence of orange colored particles. Furthermore, the dissolution of organic carbon was the lowest among the treatments, despite the largest amount of organic matter (Table 3), showing that peat contained stable organic matter with a high humification degree. By contrast, co-amendment of Fe with sludge increased soil pH to about 8 in the deeper soil layers, decreased redox potential, and increased the DOC, which at the column bottom was the highest among the treatments. Contrary to peat, sludge contains poorly humified and more soluble organic matter, which can easily spread to deeper soil layers and catalyze redox reactions (Table 7). Higher biochemical activities in the Fe+SS than in the Fe+P treatment also show that sludge has greater potential decomposition rate of OM than peat. Despite the decreased redox potential in the deeper layers of the Fe+SS, Fe solubility was relatively low (0.5 mg L^{-1}) and dissolved As concentration at the end of the experiment dropped below 0.01 mg L^{-1}, the limit concentration for drinking water. This result is somewhat different from the commonly made observation that increased soil pH can weaken As sorption onto Fe (oxy)hydroxides due to the increase in surface negative charge (Carabante et al. 2009). Possibly, the sulfidization became effective in the deepest soil layers, likely accelerated by the presence of microorganisms in the sludge, as indicated by the higher soil dehydrogenase activity (Trevors 1984). Sulfate concentration in porewater at the bottom was on average by two orders of magnitude lower than in the middle of the column indicating prerequisites for a possible sulfide formation. Visual examination of the dismantled column segments showed that deeper soil layers contained unaltered sludge characterized by a strong odor, unchanged both color and consistency of the mixture, as compared to clear oxidization in the top layer indicated by the presence of orange precipitates (Fe oxides). It is unclear though whether the possible sulfidization could have had any immobilizing effect on Fe and As. Sulfate concentration was also significantly lower in the middle and bottom layers of soil containing only Fe, where concentrations of dissolved As and Fe were the highest. Previous studies showed that formation of (iron)-arsenosulfides in soil has a narrow range of suitable thermodynamic conditions and that microbial sulfidogenesis by sulfate-reducing bacteria can markedly change Fe mineralogy and substantially increase As solubility (Burton et al. 2011). Arsenic mobilization from As(V)-co-precipitated jarosite due to abiotic sulfidization was reported by Johnston et al. (2012).

Dissolved Ca concentrations in the bottom layers of Fe-sludge columns were by one to two orders of magnitude lower than at the top layers, suggesting that decreased As solubility at the bottom might be due to its precipitation with Ca as calcium hydrogen arsenate ($CaHAsO_4$) or calcium arsenate [$Ca_3(AsO_4)_2$] (Porter et al. 2004). Similar behavior could be anticipated in soil amended with Fe- and Ca-rich ash with pH>8, where a strong positive correlation between Ca and As in porewater was observed (correlation coefficient=0.86, R^2=75 %). However, dissolved As concentrations (0.3–1.5 mg L^{-1}) were considerably above the drinking water limit. Arsenic concentrations in aqueous solutions in equilibrium with calcium arsenates reported in literature are very high ranging from tens of milligrams per liter to several grams per liter (Magalhães 2002; Donahue and Hendry 2003; Zhu et al. 2006), which are too high to consider precipitation of Ca-arsenates as a feasible long-term As immobilization measure. One particular feature observed in this soil mixture was the absence of any signs of Fe oxidation even in the top layer. Iron corrosion is known to be inhibited at high pH range (Silverman et al. 1995) indicating that iron efficiency to sorb contaminants might be hindered by alkaline ash amendment. Ashes have highly variable composition and the results might differ substantially if other type or aged (lower pH) ashes were used.

Gypsum co-amendment was the second most efficient treatment after Fe+P. Despite the high Ca concentration added to soil with gypsum, no correlation between dissolved As and Ca was observed. This is hardly surprising in view of the low abundance of As in comparison to that of gypsum together with the relatively high solubility of gypsum. There was a slight decrease in redox and certain dissolution of Fe and As at the bottom, but less than in untreated soil and especially compared to Fe-treated soil. High concentration of dissolved sulfate, which is considered as a competing oxyanion for sorption sites (Wilkie and Hering 1996), seems to have insignificant interference with As sorption. Jain and Loeppert (2000) also reported no influence of sulfate on arsenate adsorption to ferrihydrite over a broad range of pH and As/S molar ratios. Co-addition of gypsum lowered soil density, thus improving air diffusion into the column and possibly increasing Fe–As stability.

Suitability of treated soil for landfill top cover

Each layer of the landfill top cover has a purpose. The function of the vegetation and protection layers, which are the uppermost layers of the landfill cover, is to protect the barrier below against freezing and desiccation, to store water and reduce percolation, and to sustain vegetation growth so that the landfill surface is protected against erosion. This means that suitable physicochemical characteristics of soil

should be complemented with favorable biological functions, including low soil toxicity. Although the untreated soil showed moderate toxicity to bacteria, soil treatment further decreased the soil toxicity. It is important to underline that the used biotoxicity test accounts for toxicity associated to both solid and liquid soil phases.

All mixtures containing Fe together with co-amendments increased the WHC, which confirms that an improvement of soil physical, chemical, and microbiogical properties may require a combination of soil amendments rather than the addition of Fe alone. Increased soil WHC improves water supply to plants, minimizes the amount of water that reaches the liner and, along with reduced soil toxicity, and keeps the biogeochemical cycles active. The highest WHC was achieved in Fe+SS and Fe+P treatments. Soil metabolic functions as indicated by the higher hydrolase and dehydrogenase activities and ATP contents showed that these two amendment combinations can best stimulate the soil metabolic functions. However, Fe+SS was the mixture that initially had the highest EC, which is an indication of dissolved ions and salts. Soil salinity can be a limitation for the vegetation establishment. The EC at the top layer is expected to decrease over time as shown by this column test, but an immediate sow of this soil mixture with plant seeds might cause a failure in seed germination. Some countries include EC among the soil characteristics that have established limit values for vegetation layer, e.g., in Germany it is <0.5 mS cm^{-1} (Depvereinf 2009). In this regard, the Fe+P treatment may be a more suitable option. Furthermore, significantly increased urease activity indicates a higher fraction of plant available N (He et al. 2010) present in this mixture. Although soil with Fe+SS had on average a higher urease activity than Fe+P treatment, this difference was significant only in the deepest layer where sludge was still in its initial (nondecomposed) state.

An important function of a landfill top cover is to minimize landfill gas (LFG) emissions. Usually, the liner is the main barrier for LFG emissions. However, minor amounts diffusing through the liner should be taken care of by the upper layers of the cover construction, i.e., the soil. A higher microbial activity in the soil, which can be provided by high organic matter content, increases the methane oxidation, reducing LFG emissions from landfills. However, when LFG contacts oxygen closer to the surface, the biodegradable gases get biologically oxidized, leading to sludge formation (about 40 % of the CH$_4$ will be utilized for cell formation); thus, the structure of the soil might change, pore sizes diminish, and the gas exchange with the atmosphere would decrease. Using As-containing soil for a landfill cover should therefore be considered for landfills with low LFG generation potential.

Conclusions

Soil amendment with iron alone once again showed to be highly effective for As immobilization (99 % efficiency), but only in the upper soil layer (down to a half a meter). It is shown that the slightly reduced soil conditions in deeper layers substantially increases the risk for As dissolution. Therefore, the selection of soil amendments and the suitability of chemically stabilized As-contaminated soil for the landfill cover depend on the intended thickness of the top layer.

For As to be stable in thicker soil layers, a combination of amendments that can help to keep soil porous and ensure the air diffusion through the entire depth of the top layer of the landfill cover may be required. The most suitable combination of soil amendments that satisfied this condition was co-amendment of iron and peat. Besides no observed toxicity to bacteria, dissolved As concentration in porewater of this soil mixture in most cases was below the drinking water limit. Soil amendment with iron and gypsum was nearly as efficient as Fe+P, and this is most likely the result of a low soil density and good air diffusion to the soil profile.

The least suitable combination of soil amendments for As immobilization was a mixture of iron with coal fly ash. In addition to the low WHC and the high soil density, this amendment combination increased As solubility throughout the soil profile.

Co-addition of soil ameliorating materials, particularly those containing organic matter, improved soil biochemical properties as shown by the increased enzyme activities. Although soil microbial biomass and activity was at relatively low levels in all treatments, the onset of specific microbial functional groups influencing the As speciation such as S-, Fe-, Mn-, reducing- and nitrogen-fixing bacteria, favored by the reduced As toxicity and soil amelioration, should be monitored in field. Such microbial groups may alter specific mineral phases and change As fractionation in soil.

The establishment of a pilot scale field experiment, including plant tests, is in progress to validate and supplement the laboratory results.

If excavation of contaminated soil is continued to be the main remediation technique, selection of a proper combination of amendments for As immobilization can offer an alternative solution to landfilling. The treated soil used as a secondary construction material in landfill covers might considerably reduce the demand for landfill capacity and clean soil as well as reduce the costs for landfilling.

References

Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS (2004) Role of assisted natural remediation in environmental cleanup. Geoderma 122:121–142

Burton ED, Johnston SG, Bush RT (2011) Microbial sulfidogenesis in ferrihydrite-rich environments: effects on iron mineralogy and arsenic mobility. Geochim Cosmochim Ac 75:3072–3087

Carabante I, Grahn M, Holmgren A, Kumpiene J, Hedlund J (2009) Adsorption of As(V) on iron oxide nanoparticle films studied by in situ ATR-FTIR spectroscopy. Colloid Surface A 346:106–113

Ciardi C, Nannipieri P (1990) A comparison of methods for measuring ATP in soil. Soil Biol Biochem 22:725–727

Ciavatta C, Govi M, Vittori Antisari L, Sequi P (1990) Charac-1999. Characterization of humified compounds by extraction and fractionation fractions and the humification indices of different organic wastes on solid polyvinilpyrrolidone. J Chromatogr 509:141–146

Coeurdassier M, Scheifler R, Mench M, Crini N, Vangronsveld J, de Vaufleury A (2010) Arsenic transfer and impacts on snails exposed to stabilized and untreated As-contaminated soils. Environ Pollut 158:2078–2083

2003/33/EC Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Official Journal L 11, 16.1.2003

Donahue R, Hendry MJ (2003) Geochemistry of arsenic in uranium mine mill tailings, Saskatchewan, Canada. Appl Geochem 18:1733–1750

Depvereinf V (2009) Verordnung zur Vereinfachung des Deponierechts (Deponievereinfachungsverordnung—DepvereinfV), BGBl. I S. 897, 29/04/2009

Geroni JN, Bowell RJ, Dey M, Sapsford DJ, Williams KP (2009) Removal of arsenic (III) from contaminated waters using iron (ii) and citrate. Proceedings of the 8th International Conference on Acid Rock Drainage (ICARD) and securing the future: mining, metals & the environment in a sustainable society 2009, 22–26 June 2009, Skelleftea, Sweden, p 739–747

Hartley W, Lepp NW (2008) Effect of in situ soil amendments on arsenic uptake in successive harvests of ryegrass (*Lolium perenne* cv Elka) grown in amended As-polluted soils. Environ Pollut 156:1030–1040

He Z, Honeycutt CH, Griffin TS, Larkin RP, Olanya M, Halloran JM (2010) Increases of soil phosphatase and urease activities in potato fields by cropping rotation practices. J Food Agriculture & Environment 8:1112–1117

Jain A, Loeppert RH (2000) Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J Environ Qual 29:1422–1430

Johnston SG, Burton ED, Keene AF, Planer-Friedrich B, Voegelin A, Blackford MG, Lumpkin GR (2012) Arsenic mobilization and iron transformations during sulfidization of As(V)-bearing jarosite. Chem Geol 334:9–24. doi:10.1016/j.chemgeo.2012.09.045

Kumpiene J, Ragnvaldsson D, Lövgren L, Tesfalidet S, Gustavsson B, Lättström A, Leffler P, Maurice C (2009) Impact of water saturation level on arsenic and metal mobility in the Fe-amended soil. Chemosphere 74:206–215

Lappalainen J, Juvonen R, Vaajasaari K, Karp M (1999) A new flash method for measuring the toxicity of solid and colored samples. Chemosphere 38:1065–108

Lavkulich LM (1981) Exchangeable cations and total exchangeable capacity by the ammonium acetate method at pH 7.0. In: Carter MR (ed) 1993, Soil sampling and methods of analysis. Lewis Publishers, Boca Raton, FL

Magalhães MCF (2002) Arsenic. An environmental problem limited by solubility. Pure Appl Chem 74:1843–1850

Mench M, Vangronsveld J, Beckx C, Ruttens A (2006) Progress in assisted natural remediation of an arsenic contaminated agricultural soil. Environ Pollut 144:51–61

Nannipieri P, Ceccanti B, Cervelli S, Sequi P (1974) Use of 0.1 M pyrophosphate to extract urease from a podzol. Soil Biol Biochem 6:359–362

Nielsen SS, Petersen LR, Kjeldsen P, Jakobsen R (2011) Amendment of arsenic and chromium polluted soil from wood preservation by iron residues from water treatment. Chemosphere 84:383–389

Pedersen HD, Postma D, Jakobsen R (2006) Release of arsenic associated with the reduction and transformation of iron oxides. Geochim Cosmochim Acta 70:4116–4129

Porter SK, Scheckel KG, Impellitteri CA, Ryan JA (2004) Toxic metals in the environment: thermodynamic considerations for possible immobilisation strategies for Pb, Cd, As, and Hg. Crit Rev Env Sci Tec 34:495–604

Renella G, Landi L, Ascher J, Ceccherini MT, Pietramellara G, Mench M, Nannipieri P (2008) Long-term effects of aided phytostabilisation of trace elements on microbial biomass and activity, enzyme activities, and composition of microbial community in the Jales contaminated mine spoils. Environ Pollut 152:702–712

Ruttens A, Mench M, Colpaert JV, Boisson J, Carleer R, Vangronsveld J (2006) Phytostabilization of a metal contaminated sandy soil. I: Influence of compost and/or inorganic metal immobilizing soil amendments on phytotoxicity and plant availability of metals. Environ Pollut 144:524–532

Silverman DC, Kalota DJ, Stover FS (1995) Effect of pH on corrosion inhibition of steel by polyaspartic acid. Corrosion 51:818–825

Soon YK, Abboud S (1991) A comparison of some methods for soil organic carbon determination. Commun Soil Sci Plant Anal 22:943–954

Tabatabai MA (1982) Methods of soil analysis. Part 2: chemical and microbiological properties. In: Page AL, Miller RH, Keeney DR (eds) Soil enzymes. Soil Science of America, Madison, pp 907–943

Tabatabai MA, Bremner JM (1969) Use of p-nitrophenyl phosphate for assay of soil phosphatase activity. Soil Biol Biochem 1:301–307

Trevors JT (1984) Effect of substrate concentration, inorganic nitrogen, concentration, temperature and pH on dehydrogenase activity in soil. Plant Soil 77:285–293

WHO (1993) Guidelines for drinking-water quality, 2nd edn, vol 1—recommendations. WHO, Geneva

Wilkie JA, Hering JG (1996) Adsorption of arsenic into hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. Colloid Surf A 107:97–110

Zhu YN, Zhang XH, Xie QL, Wang DQ, Cheng GW (2006) Solubility and stability of calcium arsenates at 25°C. Water Air Soil Poll 169:221–238

Zornoza R, Landi L, Nannipieri P, Renella G (2009) A protocol for the assay of arylesterase activity in soil. Soil Biol Biochem 41:659–662